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*SEMI ANNUAL TECHNICAL REPORT FOR THE PERIOD  
2 May 1971 to 2 November 1971*

**INVESTIGATION OF THE INFLUENCE OF STRUCTURE ON  
CHEMICAL STABILITY AND THERMAL/MECHANICAL  
SHOCK PROPERTIES OF GLASS-LIKE CARBONS**

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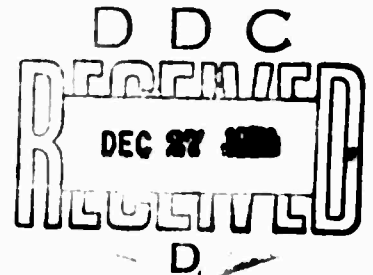
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CHEMICAL STABILITY AND THERMAL/MECHANICAL  
SHOCK PROPERTIES OF GLASS-LIKE CARBONS

SUMMARY

A systematic investigation of the properties of glass-like carbons is needed if these materials are to be effectively used in our advancing technology. This study was instituted to investigate the chemical reactivity and thermal and mechanical shock behavior of glass-like carbons and to correlate these properties with observable structural features. Reactivity studies were selected for initial work because glass-like carbons appear to have unusual chemical stability compared to other carbon forms and this stability is an important parameter in most high temperature applications. Shock property measurements were incorporated into the program to gain an insight into a potential weakness of glass-like carbon. Although not nearly so shock resistant as graphite, glass-like carbon does appear to have sufficient shock resistance to withstand substantial thermal and mechanical stresses.

During the first six months of this program, we have performed work in the following areas: (1) Chemical Stability, (2) Thermal Shock Testing, (3) Microhardness Testing, (4) Surface Energy and Work of Fracture. In addition, necessary work on sample characterization and microstructural investigations were carried out to enable a correlation of properties with structure.

During this reporting period, the reactivity studies were limited to rate measurements of various carbon forms with oxygen. Rate measurements have been conducted on two types of glass-like carbons ("Glassy" carbon produced by Tokai Electrode Manufacturing Company, Ltd., and "Carbone Vitreux" produced by Le Carbone Lorrain), an amorphous pyrocarbon produced at Gulf Energy and Environmental Systems, Inc., and a standard nuclear graphite. Rates of reaction of these carbon types varied over a factor of

nearly 3,000. The differences in rate are not nearly so dependent upon carbon type as upon heat treatment temperature. Structural investigations show that impurity content variation is a major contributor to rate variations. Rate data for these four forms of carbon are listed in Table I on Page 4.

A technique has been developed for thermal shocking glass-like carbons using a low power welding arc. Thermal shock tests have been conducted on "Carbone Vitreux" and on a porous glass-like carbon produced at the University of Michigan. Results of these experiments are not yet analyzed quantitatively, but qualitatively porous materials are more shock resistant than the non-porous materials, and increased heat treatment temperatures appear to increase the thermal shock resistance.

Techniques were also developed for measuring mechanical shock using a hardness measuring device. Acoustic emission monitoring has proven valuable in obtaining a real-time indication of crack initiation and propagation. Measurements have been made on the shock resistance of three types of glass-like carbons as listed in Table II on Page 11.

A quantitative measure of the shock resistance of glass-like carbons is being obtained by determining the surface energy and work of fracture. Standard techniques for brittle materials are being used for these studies as given on Page 13. All measurements during this period have been conducted on "Carbone Vitreux," the Le Carbone Lorraine produced material. Results show that both the work of fracture and fracture surface energy are substantially higher than those of glass. Also, work of fracture was shown to decrease with heat treatment temperature.

Sample characterization during this reporting period has centered around microscopic examination using both scanning electron and optical microscopy. Micrographs of the various glass-like carbon types are shown in Figures 12 through 26.



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INTRODUCTION

During this period, work has been performed in the following five areas:

- I. Chemical Stability.
- II. Thermal Shock Testing.
- III. Microhardness Testing.
- IV. Surface Energy and Work of Fracture Measurements.
- V. Sample Characterization.

Details of our progress in these areas are given in the following sections of the report.

During this work, we have investigated several materials: three glass-like carbon materials - one produced by Tokai Electrode Manufacturing Company, Ltd., called "Glassy" carbon; another produced by Le Carbone Lorraine called "Carbone Vitreux;" and the third produced by Prof. Hucke's group at the University of Michigan, under ARPA Contract, hereafter referred to as porous glass-like carbon.

In addition, an amorphous pyrocarbon produced by Gulf Energy and Environmental Systems, Inc., also under ARPA Contract, has been investigated. This material is referred to as vapor deposited carbon throughout the report.

I. CHEMICAL STABILITY OF GLASS-LIKE CARBONS

When glass-like carbons were first reported, scientists were intrigued with their properties, namely, low density, impermeability to gases, low thermal conductivity, high strength, etc. The fact that these materials have such a low permeability suggested the potential for



an unusually low reactivity to oxidizing gases. In 1962, Davidson<sup>(1)</sup> reported that the reaction of carbon dioxide with glass-like carbon produced by General Electric Company, Ltd., proceeded at a rate 1/20th that of electrode graphites at temperatures from 600 to 1000°C. In addition, he pointed out that the rate of reaction decreases with an increase in a final heat treatment temperature. In that same year, Yamada and Sato<sup>(2)</sup> reported that the Tokai Electrode produced "Glassy" carbon reacted with air at a rate of about one-third that of normal graphite at 800°C.

Other workers<sup>(3-5)</sup> have also shown that glass-like carbons are less reactive than other carbon forms. With the exception of the work of J. C. Lewis<sup>(4)</sup> and Higgins and Antill,<sup>(3)</sup> the studies have been qualitative under conditions which are not conducive to direct comparisons between the various materials.

It is the intent of this study to investigate a series of glass-like carbon types under well defined conditions so that rate constants including temperature coefficients, may be determined and directly compared.

### Experimental Approach

During this report period, reactivity measurements have been made on four types of carbon as follows:

- (1) TSX - nuclear graphite.
- (2) Tokai Electrode Manufacturing Company, Ltd., "Glassy" carbon.
- (3) "Carbone Vitreux" produced by Le Carbone Lorraine.
- (4) Low temperature, vapor-deposited pyrocarbon ("LTI Pyrolyte") produced by Gulf Energy and Environmental Systems, Inc., under ARPA contract.

TSX nuclear graphite, used as a reference for this work, is a very pure fine-grained needle coke graphite with a reported ash content of about 10-100 ppm.

The "glassy" carbon samples from Tokai were supplied in three grades, GC-10, GC-20, and GC-30. Heat treatment temperatures and other selected properties of the samples are shown in Table I.

Only one grade of "carbone vitreux" was purchased, but some of the material was heat treated in our laboratory to 2000 and 2900°C.

The low temperature vapor deposited pyrocarbon was supplied by Dr. J. C. Bokros of Gulf Energy and Environmental Systems, Inc.

Except for the vapor deposited carbon, samples 13 mm by 38 mm by 2 to 3 mm thick were prepared, cleaned ultrasonically, and placed in the reaction vessel. The vapor deposited samples were thin disks 20 mm in diameter by 2 mm thick.

Flowing oxygen (99.995% purity) was passed over the samples at temperatures varying from 300 to 750°C depending upon the sample reactivity.

The weight change of the samples was determined continuously by a semi-micro recording balance with a sensitivity of 1 mg per inch on the chart. The samples were suspended from the balance on a fine quartz rod in a quartz reaction vessel. There was no evidence that a catalytic reaction occurred at the point where the quartz rod contacted the sample. The temperature was controlled at  $\pm 2^\circ\text{C}$  and continuously recorded. Rates of oxidation were determined as a function of temperature and total amount of oxidation.

### Results and Conclusions

The results of the rate measurements are shown in Table I. The rate constants as a function of temperature are given in units of weight removed per unit weight of the sample per hour for one atmosphere of flowing oxygen. Figures 1 and 2 show the rates of the various carbon types as a function of temperature.

Since there is a significant variation in the apparent activation energy along with a compensating variation in frequency factor, the rates for the various carbon types at 800°K (527°C) are listed for comparison.

TABLE I. Reactivities of Carbons Tested.

| Carbon Type                 | Heat Treatment Temperature °C | Density g/cm <sup>3</sup> | Ash Content ppm | Rate Constant g/g-hour           | Rate at 800°C g/g-hour |
|-----------------------------|-------------------------------|---------------------------|-----------------|----------------------------------|------------------------|
| TSX - Nuclear Graphite      | 3000                          | 1.71                      | 10-100          | $3.4 \times 10^9 e^{-42,700/RT}$ | $7.3 \times 10^{-3}$   |
| Tokai - Glassy Carbon GC-10 | 1000                          | 1.49                      | 1000-2000       | $6.2 \times 10^6 e^{-32,000/RT}$ | $11.0 \times 10^{-3}$  |
| GC-20                       | 2000                          | 1.48                      | 1000-2000       | $3.2 \times 10^4 e^{-23,600/RT}$ | $11.0 \times 10^{-3}$  |
| GC-30 (0-6% Oxidation)      | 3000                          | 1.45                      | 70-100          | $5.4 \times 10^3 e^{-24,000/RT}$ | $1.5 \times 10^{-3}$   |
| GC-30 (17% Oxidation)       | 3000                          |                           |                 | $2.5 \times 10^5 e^{-33,500/RT}$ | $0.18 \times 10^{-3}$  |
| Carbone Vitreux V-1         | 1000                          | 1.5                       | 200             | $1.9 \times 10^7 e^{-28,600/RT}$ | $290 \times 10^{-3}$   |
| V-2                         | 2000                          | --                        | --              | $3.5 \times 10^6 e^{-35,000/RT}$ | $0.96 \times 10^{-3}$  |
| V-3                         | 2900                          | --                        | --              | $7.6 \times 10^6 e^{-38,800/RT}$ | $0.19 \times 10^{-3}$  |
| LTI Pyrolyte 5408-17        | < 1500                        | 1.46                      | --              | $3.2 \times 10^9 e^{-35,900/RT}$ | $497 \times 10^{-3}$   |

These rates vary from  $0.18 \times 10^{-3}$  to  $497 \times 10^{-3}$  grams carbon removed/gram of sample-hour (g/g-hr). This variation is highly affected by heat treatment. "Glassy" carbon and "Carbone Vitreux" samples show a large decrease in reactivity with increasing heat treatment temperature. This decrease can be partially explained by a decreasing impurity level, but further correlation with impurity concentration is required to fully understand the decreasing rate.

In general, glass-like carbon samples with low reactivity appear to show a decreasing rate as the extend of oxidation increases. This is shown in Table I by comparing the rate of GC-30 in the range of 0-6% oxidation with that of the same sample after 17% oxidation. This phenomenon is also observed for other samples with low reactivity but the samples heat treated at 2000°C or below tend to follow the normal trend of increasing oxidation rate as the reaction proceeds. At present, although this is clearly a real effect, we have no explanation for the behavior.

#### Morphological Changes during Oxidation

Microscopic examination of the oxidized samples have been compared with those of unoxidized samples. In "glassy" carbon and "Carbone Vitreux" heat treated at temperatures of 2000°C or below, a fine fluffy impurity covers the entire sample. This impurity which coats all surfaces including of pores of the sample is easily removed by dipping in water and appears to be water soluble. It is easily reformed by subsequent oxidation. Figure 3 is a micrograph of a GC-10 sample after 8 to 10% oxidation showing the impurity coated around the sample. Elemental analysis of the impurity revealed that the major components were calcium, sulfur, aluminum, silicon, potassium, and iron.

After heat treatment to 3000°C, no impurity is observed following the oxidation; on the contrary the samples remain clean and have a glass-like appearance. However, they are pitted severely due to a highly selective attack. Figure 4 shows a comparison of a scanning electron micrograph of the surface of a GC-30 sample prior to oxidation with that of a sample after 2% oxidation. It can be seen from this figure that some of the major structural imperfections in the sample lead to large pits. On the other hand, the small

pits are not readily identified with any clear structural feature in the unreacted sample.

It is obvious from this data that the reactivity of glass-like carbon is highly dependent upon the structure of the material and future experiments will be directed to understanding this variability.

## II. THERMAL SHOCK TESTING OF GLASS-LIKE CARBONS

The thermal shock properties of glass-like carbons, as reported in the literature, are in qualitative terms and are expressed as a temperature from which the material can be quenched in water without breaking. Even these data are quite limited,<sup>(6)</sup> and the testing is strictly applicable only for quenching of heated objects in water.

The objective of this work is to describe the thermal shock behavior more quantitatively and to describe the details of the thermal shock process by using the real-time information available through acoustic emission monitoring.

### Experimental

The objective above imposed two restrictions on the thermal shock apparatus, namely: (1) that the conditions of heat transfer be well-defined and amenable to analysis, and (2) that the method used generate no spurious high-frequency (0.1-1 MHz) sounds which would interfere with acoustic emission monitoring. Our initial efforts were thus devoted to developing a technique for thermal shocking glass-like carbon within these limits.

The fact that commercial glass-like carbon is available in thicknesses of not greater than 1/8 inch severely restricts the choice of shock methods. Immersion of a sample of this thickness into any fluid dictates that heat transfer occurs mainly across the faces perpendicular to the 1/8 inch dimension. The Biot modulus necessary to obtain any temperature gradient between the surface of a sample and its interior is about 0.1.

The Biot modulus is defined as  $\bar{h} L/K$ , where  $\bar{h}$  = surface transfer coefficient,  $L$  = half thickness of plate (1/16 in.), and  $K$  = thermal conductivity. Thus, for a reasonable thermal shock,  $\bar{h}$  should be of the order 1000 to 10,000 BTU/hr-ft<sup>2</sup> °F. These high surface heat transfer coefficients are obtained with boiling water and, marginally, with liquid metals. It has been shown<sup>(6)</sup> that a water quench from about 1000°C will fracture glass-like carbon. However, the boiling produces high frequency noise and thus violates requirement (2) above.

Liquid metal heat transfer was attempted, without success. Liquid tin was used as a quench medium because of its good oxidation resistance. Thermal shocks produced by quenching 1200°C carbon samples into molten tin at 235°C or by heating samples from liquid nitrogen temperature to 1000°C in tin were insufficient to fracture the samples, so this approach was abandoned.

Recently, Yahr<sup>(7)</sup> reported successfully thermal shocking graphite discs using an inert-gas welder. The discs failed from the tensile stresses generated at their outer surfaces. Since this method produced thermal shocks severe enough to fracture graphite, it was assumed that it would be workable for glass-like carbons. Initial experiments showed that a low-power welding arc was sufficient to fracture small pieces (ca. 3/4 in.) of glass-like carbon. Accordingly, a system was assembled. The apparatus consisted of a small arc welder\* with a welding current range of 0.25 to 25 amperes, together with a magnetic table for the machinist's vise used to hold the sample and the micrometer drive used for the welding torch.

The sample, in the form of a disc, was clamped in the machinist's vise. The vise included the acoustic emission transducer which was pressure coupled to the sample with a 1/16 in. disc of silicone sealant. The micrometer driven torch struck the sample at its center. The acoustic emission signals generated during testing traveled through the couplant with little loss to the transducer, and then to the acoustic emission monitoring equipment which is described in the Appendix.

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\* Model UTW-14, Vacuum Tube Products.

Surprisingly, an electric arc welder does not generate sufficient noise to interfere with the acoustic emission monitor. While the high frequency starter signal was a great source of noise, a stable arc, once formed, was not. The best means for starting the arc and the conditions for a stable arc were determined experimentally.

The sample size was also a critical part of the testing. The minimum disc size was determined by the need to protect the transducer from excessive heat, and the maximum size was determined by the power available from the welder. Yahr,<sup>(7)</sup> for instance, found that 3/4 in. discs of many graphites broke so easily that his test was not sufficiently sensitive, while many 4 in. discs could not be broken by his welder, which was rated at up to 20,000 watts so he used a 2 in. diameter disc. In many of the initial tests on glass-like carbon, 1-1/2 in. diameter discs were used, but occasional difficulties in fracturing them plus the desirability of conserving material led to the adoption of a disc 1 in. in diameter. A carbon standoff, cemented to the disc with graphite cement,\* was provided to protect the transducer.

### Experimental Results

Essentially all of the experimental work done thus far was performed on "Carbone Vitreux" originally heat treated to 1000°C. Some samples of this material were then heat treated at 2000°C and 2900°C to supply material for thermal shock, mechanical testing, and kinetic studies. In order to conserve material, initial work was performed on strips of 1000°C heat treated carbon 0.375 in. wide x 0.071 in. thick x 2 in. long. Thermal shocking was done in the middle of the 0.375 in. x 2 in. faces, at a power of 60-130 watts. The work showed that: (1) acoustic emissions received during testing correlated well with observed cracks; (2) the cracks were produced on cooling rather than on heating, most of them immediately after power shutdown; (3) in cases when the arc was of insufficient power to cause fracture, the samples always broke through the shocked zone when tested by bending. Even when a sample was shocked in three different locations, the crack passed through all shocked zones, indicating the presence of substantial residual stress.

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\* Great Lake Carbon Company., P-514 graphite cement.



In order to more thoroughly document these effects, another experiment was done. Seventeen strips like those described above were cut and heat treated to 2000°C. Five of the samples were used as controls and the other 12 were tested at a power below that required to cause cracking, about 60 watts. However, due to sample to sample differences, several of the samples contained small cracks which correlated well with the acoustic emission record even at this low power. Half of the tested samples were again annealed at 2000°C, and the whole group was tested in four-point bending so that a substantial length of the sample (1-1/8 in.) including the shocked zone would be in the same state of tension. The following observations were made:

- (1) The bars always broke at the location of the arc.
- (2) Strength was reduced to 60% of the control strength. Annealed samples recovered to 87% of control strength.

A limited amount of testing has been done on 1 in. diameter discs. The results of these tests were:

- (1) 200 watts was the approximate threshold power for fracture of "Carbone Vitreux" processed at 1000°C; below this power, small cracks appeared immediately under the arc on cooling. See Figure 5.
- (2) The sample heat treated to 2900°C did not fracture at powers up to 200 watts. No cracking appeared on any of these samples. See Figure 6.
- (3) A few samples of porous carbon provided by Hucke at the University of Michigan and processed to 2000°C were tested. These had good resistance to thermal shock and did not exhibit cracks on cooling. The samples tested at approximately 200 watts broke in half, but these samples were only 3/4 in. in outside diameter so no direct comparison can be made.

A great deal more testing, along with a quantitative analysis, will be necessary before the objective of this portion of the program is met. The presence of center cracks in 1000°C carbon and its absence in 2900°C material is noteworthy. Although thermal shock coefficients show that the higher temperature material should be more shock resistant, differences in properties

are not great. Since the carbon directly under the arc is placed in compression during heating, perhaps a permanent strain takes place which does not occur in 2900°C material. The strain would cause the center portion to be placed in tension on cooldown, and may explain the observed cracking.

### Conclusions

1. The threshold power necessary to fracture 3/4 in. discs of 1000°C Carbone Vitreux in our apparatus is about 200 watts.
2. Carbone Vitreux processed to 2900°C is more resistant to thermal shock by an undetermined amount. Future experiment will clarify this effect.

### III. MONITORED MICROHARDNESS TESTING OF GLASS-LIKE CARBONS

In theory, it would be instructive to "listen" sensitively to a brittle material as it undergoes deformation or fracture by a diamond indenter. This monitoring is expected to provide information on the point loads causing microfracture and, if the size of the fracture event can be determined, may provide a quantitative relationship between micro-damage and the resulting acoustic emissions.

### Experimental

A commercial hardness tester\* equipped with Diamond Pyramid Hardness (DPH) and Knoop diamond indenters was used for this work. A transducer was clamped to the sample, which was in the form of a polished metallographic sample. A liquid shear couplant\*\* was used to conduct the signals to the transducer with little loss. The hardness tester utilized a standard load cycle in which the sample was brought into contact with the loaded diamond indenter at a fixed rate for a fixed length of time and then lowered at a fixed rate. The relays necessary to accomplish this all generated substantial spurious noise. After several attempts

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\* Tukson Tester, Wilson Mechanical Div., American Chain and Cable Company.

\*\* Dow Resin No. 276-V9 Shear Couplant.

to eliminate this noise, a simple means of using the machine in a way that bypassed the relays was devised. This was apparently successful, because the indenter could be replaced in an indentation very accurately, leaving no second mark.

### Results and Discussion

Results are included in Table II below. All measurements were made with DPH indenter at a load of 4 kg.

TABLE II. Summary of Monitored Microhardness Testing Results

| <u>Sample Type</u> | <u>No. of Acoustic Emissions (average)</u> | <u>Length of Indent Diagonal microns</u> |
|--------------------|--|--|
| GC-10*             | 144  | 150                                      |
| V-10               | 82   | 200                                      |
| 317-39A            | 47   | 325                                      |

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\* Glassy Carbon made by Tokai Electrode, Ltd.

\*\* Carbone Vitreux made by Le Carbone Lorraine.

\*\*\* Porous carbon supplied by University of Michigan.

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The acoustic values are averages; there is a rather high degree of scatter in the results. This may be a statistical effect due to the very small volume under test. Judging by the diagonal length (and, thus, the size of the indenter), there seems no apparent relationship between indent size and acoustic emission data.

Figures 7, 8, and 9 show the three materials, all indented at the same load. Although the porous carbon appears to be least severely cracked, which agrees with acoustic data, there is no observable difference between the GC-10 and V-10 micrographs which would account for the factor of two difference in the acoustic data.

The depth of the cracks has thus far not been determined, but this depth might help explain some of the differences noted. Attempts to polish into the indentations have thus far failed because samples have been polished too far. However, the cracks are less than 20 microns deep.

The following expected trends were verified with other materials

- (1) Pure deformation without fracture produced no emission, as demonstrated with plastics.
- (2) Metals produced some emission activity, with no cracking.
- (3) Glass developed microcracks and produced emission apparently completely due to fracture.

#### IV. EFFECTIVE SURFACE ENERGY AND WORK OF FRACTURE MEASUREMENTS

The effective surface energy is a property of fundamental importance in determining the mechanical properties of brittle materials. It is defined as the work required to create unit area of new fracture surface, not taking into account the fine-scale surface irregularities of the fracture face. In these experiments, three parameters closely related to the fracture process were measured; the fracture surface energy and the critical stress intensity factor were measured by the double-cantilever beam method, and the work of fracture was measured by three-point bending of a notched beam. In both of these methods, additional information was made available by the use of acoustic emission monitoring.

##### Experimental

The sample configurations are shown in Figures 10 and 11. All loading was done in an Instron testing machine, at a rate of 0.002 in./min. The samples loaded in tension were loaded via a chain to minimize torque. In the work-of-fracture (WOF) testing, the depth of the original notch is important;<sup>(8)</sup> the deeper the notch, the more controlled the fracture and the less energy expended in processes other than sample fracture. All work reported here was done on "Carbone Vitreux" heat treated at 1000, 2000, and 2900°C. After some preliminary testing in which the decrease in

WOF was noted, crack depth was held at 0.5 d. The work of fracture was calculated by determining the area under the load-deflection curve (by weighing) and dividing this by the area of the fracture.

Acoustic emission monitoring was performed during WOF and fracture surface energy testing by clipping a spring-loaded transducer to the specimen and using the shear couplant described in the previous section to bridge the gap between transducer and specimen. The rest of the systems is described in the Appendix.

The fracture surface energy and critical stress intensity factors were determined using the double cantilever-beam configuration shown in Figure 11. In this experiment, the load was measured as a crack was propagated along the notch shown. Prior to each propagation, which was usually 1/16 in. to 1/8 in., the position of the crack tip was defined by measuring with a travelling microscope. Locating the crack tip unambiguously was difficult because of problems inherent in observing the bottom of a notch in a black material. This was alleviated by applying a 50:50 mixture of white typewriter correction fluid\* and toluene to the notch area. This material increased the reflectivity of the surface and acted as a brittle coating to further delineate the crack tip. The fracture surface energy,  $\gamma$ , and critical stress-intensity factor,  $K_{IC}$ , were calculated using the following equations:<sup>(9,10)</sup>

$$\gamma = 6 P^2 L^2 / E W t^3 [1 + 1.34 t/L + 0.45 (t/L)^2]$$

where E is Young's modulus and all other factors are defined in the figure; and

$$K_{IC} = PL/Wt^{1.5} (3.47 + 2.32 t/L).$$

---

\*Dab, Eberhard Faber.

## Results and Discussion

The work of fracture of "Carbone Vitreux" heat treated to 1000, 2000, and 2900°C is shown in Table III below:

TABLE III. Work of Fracture Results

| <u>Heat Treatment<br/>Temperature, °C</u> | <u>Work of Fracture<br/>x ergs/cm<sup>3</sup></u> |
|---|---|
| 1000                                      | $3.41 \times 10^4$                                |
| 2000                                      | $3.77 \times 10^4$                                |
| 2900                                      | $2.42 \times 10^4$                                |

The 1000°C and 2000°C values are within experimental variance of each other, but the 2900°C specimens were consistently low. This may well reflect a real brittleness effect which takes place as ordering becomes more pronounced. The observed values are between glass at  $5 \times 10^3$  ergs/cm<sup>2</sup> and polycrystalline alumina at  $4 \times 10^4$  ergs/cm<sup>2</sup>.<sup>(8)</sup>

The fracture surface energy and critical stress intensity factor have thus far been measured only on 1000°C heat treated "Carbone Vitreux." The average values obtained were  $\gamma = 25$  joules/m<sup>2</sup>, which compares to a Wiederhorn's<sup>(11)</sup> value of 4 J/m<sup>2</sup> for various glasses. Due to the more predominantly covalent bonding, one might expect a higher value of  $\gamma$ .  $K_{IC}$ , the critical stress intensity factors, averaged about  $4 \times 10^4$  N/m<sup>3/2</sup>, compared to approximately  $7 \times 10^5$  N/m<sup>3/2</sup> for glasses. This factor should be proportional to the ultimate strength of a material and may indicate a limit on the strength of glass-like carbon, below that of glass. Glass, in the presence of corrosion effects, can have a strength greater than  $10^6$  psi.

The acoustic emission monitoring performed during the testing of double cantilever beam specimens showed a large amount of activity at the tip of cracks before any observable cracking was detected. Although the loading system could detect changes in load of 0.02 lb., the acoustic emission activity was soon recognized as the best indication that a crack was propagating and the loading should be stopped. The monitoring was 1-2 orders of magnitude more sensitive than the load cell. This early warning provided

many more data points from a single sample than would have been possible without it, because individual propagations were small. The emission data will be examined relative to fracture area, to see if a correspondence exists. This will be done for both total cracking for a single sample and for single crack propagation.

### Conclusions

1. The work of fracture of "Carbone Vitreux" is substantially higher than that of glass and decreases when samples are heated to 2900°C.
2. The fracture surface energy of "Carbone Vitreux" is also higher than that of glass, but the value of the critical stress intensity factor suggests that ultimate strengths may be lower than obtainable with glass.
3. In the double cantilever beam configuration, the small crack activity at the crack tip is easily detectable by acoustic emission monitoring. Cracking in the notched beam sample is nonexistent prior to failure.

### V. SAMPLE CHARACTERIZATION

The purpose of this work is to perform microstructural examination to evaluate structure of the various materials and also to detect changes which occur during the various tests.

Samples of "Carbone Vitreux," "Glassy" carbon, and porous glass-like carbon have all been characterized by optical and scanning electron microscopy.

### Experimental

For scanning electron microscopy, fresh fracture surfaces were observed. For the optical work, samples were ground on 120-grit SiC on a belt grinder followed by grinding on a 15-micron diamond wheel. The samples were then dry ground on 2/0 and 3/0 emery paper, followed by ultrasonic cleaning. Syntron polishing on 3-micron diamond followed



for 12 hours using a pellon cloth. Polishing was completed using 1/2 micron diamond for 1 hour followed by electronic grade MgO.

### Observations

Optical micrographs of the various glass-like carbons examined are shown in Figures 12 through 16. It can be seen that the "Carbone Vitreux" (Figure 12) tends to have large pores near its center, with porosity smaller toward free surfaces becoming nonexistent at the free surfaces. This probably reflects the discharge of pores at free surfaces. Upon heating to 2000°C or above (Figure 13), the pores tend to become filled. The precise nature of the material filling the pores is not known, but it contains more Si, S, P, and Cl than the bulk material, as determined by analysis of emitted x-ray spectra. The bulk material contains approximately 1/2% impurities, the pore fillers approximately 1%. The pore filling is apparently by condensation of impurities as they move through the carbon at high temperatures. Once formed, however, the deposits are not eliminated at 2900°C. Although the original 1000°C heat treated material exhibited no optical anisotropy, that heated to 2900°C was gray and unctuous like graphite, indicating further ordering at high temperatures.

The "Glassy" carbon was all rather featureless and contained virtually no pores. The material processed at a (nominal) temperature of 3000°C was black and did not exhibit optical anisotropy as did the "Carbone Vitreux." X-ray diffraction studies will help to define the difference between the two glass-like carbons after heat treatment approaching 3000°C.

The porous materials produced at University of Michigan (Figure 15) contained pore from one to a few microns in diameter, interspersed with dense glass-like carbon which exhibited some mottling at higher magnification, indicative of structural features. The wide variety possible in this material is exemplified by comparison with Figure 16, which shows larger pores with some smaller pores present within the more dense areas.

Scanning micrography results are presented in Figures 16 through 26. It is seen that the fracture of pore-free glass-like carbons is truly

glass-like when viewed at low magnification, with hackle marks much in evidence. These marks are not observed in the porous material.

High magnification scanning electron micrographs were required to detect structural features on "glassy" carbons (Figures 16 and 17). Structural features are larger and more highly developed in samples heat treated at 3000°C than in those heat treated to only 1000°C.

"Carbone Vitreux" processed at 1000 or 2900°C is seen in Figures 19 through 22. The porosity is evident, as is its effect on the fracture path. The filling of voids, as mentioned in the optical work above, manifests itself again in Figure 22. Many of the pores contain material which protrudes when they are broken through the mid-plane.

The scanning micrographs of the porous carbons reveals that the material with fine pores (Michigan No. 317-39A) resembles a loosely sintered compact with the "grains" about the same size as the pores (Figures 23 and 24). The microstructure of the large-pored sample (Michigan No. 318-1) shows a mixture of both large and small porosity (Figure 25 and 26).

## APPENDIX

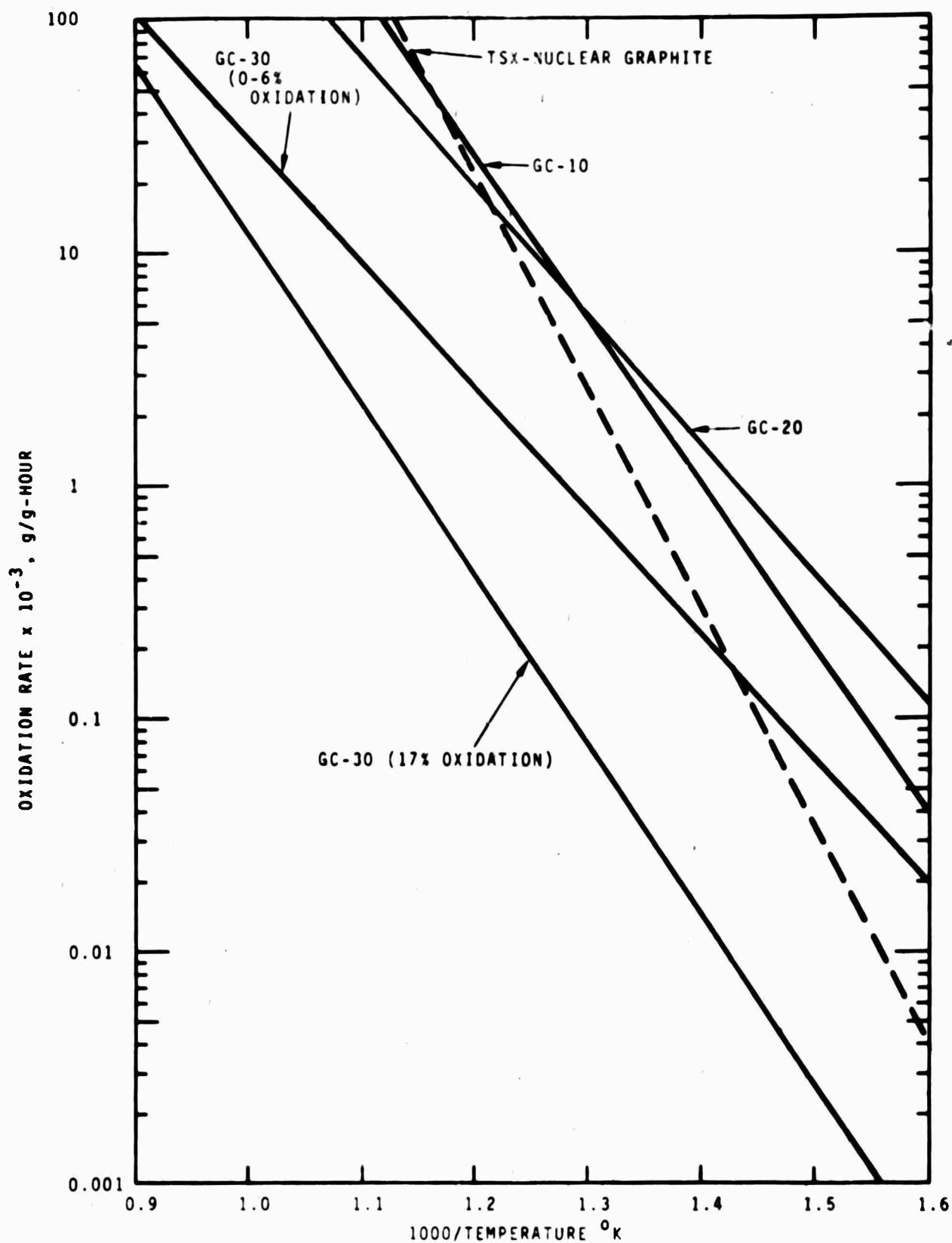
### Acoustic Emission Monitoring System

The acoustic emission monitoring system being used on the program is shown in the block diagram (Figure 27). It consists of an acoustic emission sensor, signal preamplifier, four channel acoustic emission monitor, and strip chart recorders. An oscilloscope is also used to visually monitor the acoustic emission signals.

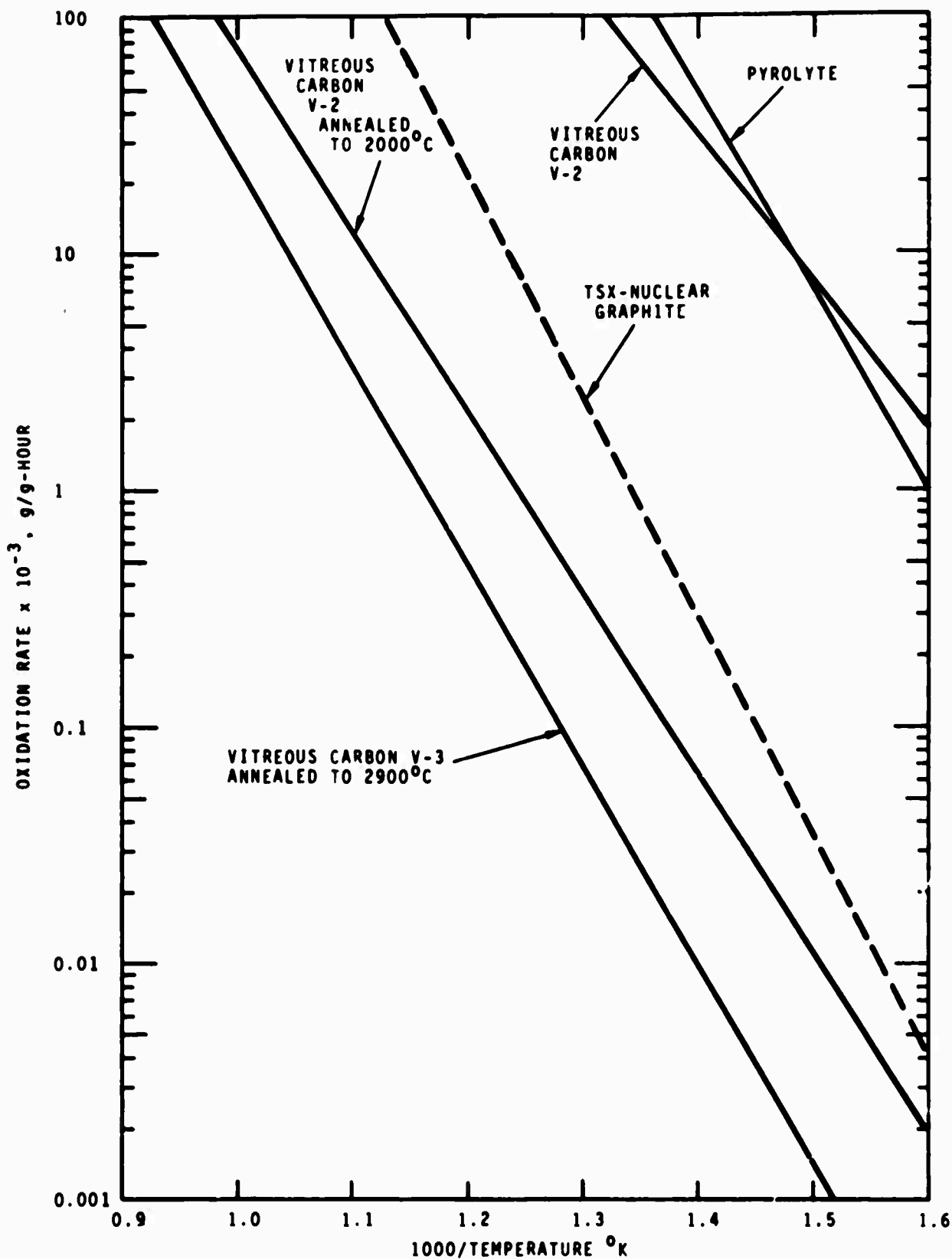
The acoustic emission sensor is normally a PZT-5A ceramic transducer mounted in a protective case, with a peak frequency response in the 600 to 800 kHz region. The output of the sensor is fed into a preamplifier tuned to a 750 kHz center frequency with a 250 kHz bandwidth. The nominal gain of the preamplifier is 100X.

The acoustic emission monitor contains four separate monitoring channels, each with a selectable high pass filter, final amplifier, count rate and totalize circuitry, and strip chart recorder drive output. On this program, a single monitoring is normally required. The high pass filter settings allow the operator to select the low frequency cut-off desired from 0Hz to 1 MHz. The final amplifier can be adjusted to provide sufficient system sensitivity. The count rate circuitry processes the input signals and produces an output proportional to the rate at which the acoustic emission signals are being received (i.e., counts/minute). The totalize circuitry produces an output which indicates the total number of acoustic emission signals received during a particular test from a sensor location. These outputs are recorded on a strip chart recorder and provide a permanent record of the test results.

The oscilloscope presentation of the amplified acoustic emission signals allows the operator to visually monitor the signals being received. An acoustic emission pulser is used during set up and calibration of the monitoring instrumentation. This pulser permits the operator to generate an acoustic emission signal of a selected amplitude and repetition rate near the expected location of actual acoustic emissions. This pulser is valuable when used to provide comparison of the results from several separate test records.

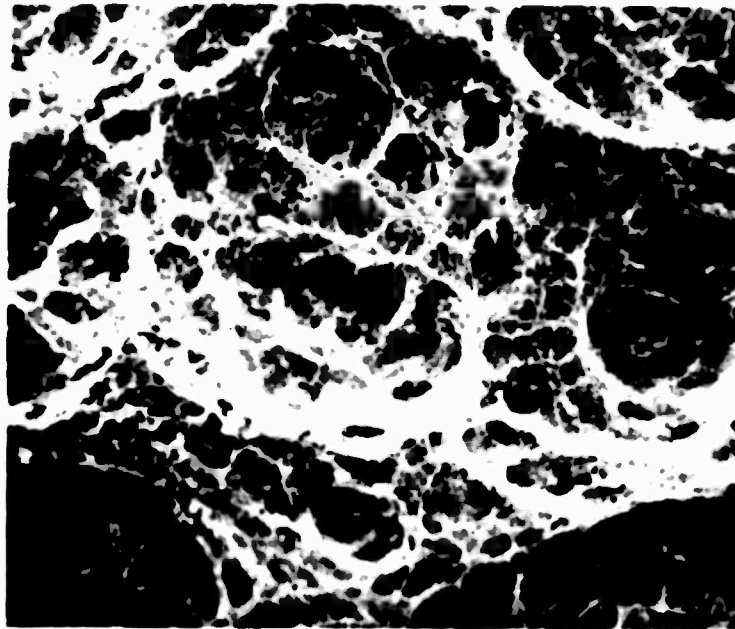


**FIGURE 1.** Rate of Oxidation of "Glassy" Carbon as a Function of Temperature.

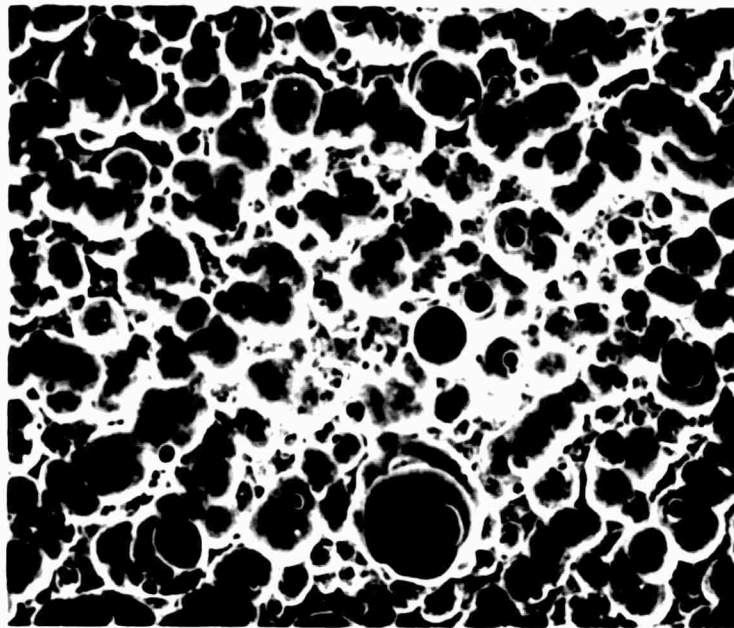


**FIGURE 2.** Rate of Oxidation of "Carbone Vitreux" and Vapor-Deposited Carbon as a Function of Temperature.

NOT REPRODUCIBLE



100X



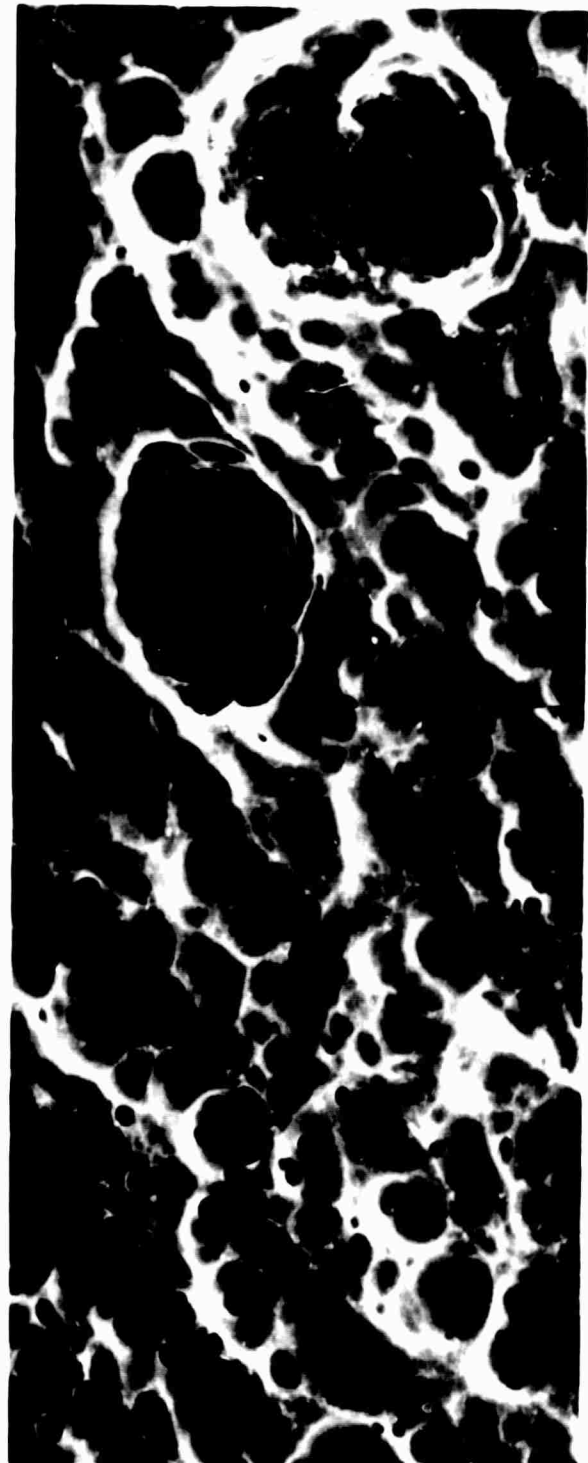
100X

**FIGURE 3.** Scanning Electron Micrographs of Oxidized "Glassy" Carbon (GC-10) showing Impurity Covering the Surface.



Before Oxidation

300X



2% Oxidized

300X

**FIGURE 4.** Scanning Electron Micrograph of "Glassy" Carbon (GC-30) Before Oxidation and After 2% Oxidation.

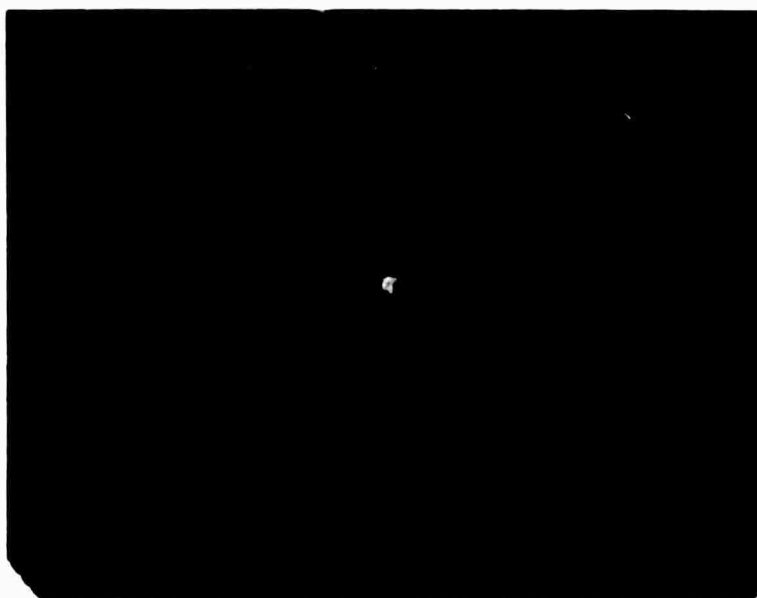


NOT REPRODUCIBLE



4.8X

FIGURE 5. Cracks near Center of 1000°C Carbone Vitreux Sample Thermally Shocked at about 180 watts, showing cracking at center.



4.8X

FIGURE 6. Complete Absence of Cracking in 2900°C Carbone Vitreux Sample Thermally Shocked at 180 watts.

NOT REPRODUCIBLE



160X

**FIGURE 7.** Micrograph showing 4 Kg Indentation in GC-10 Material.



160X

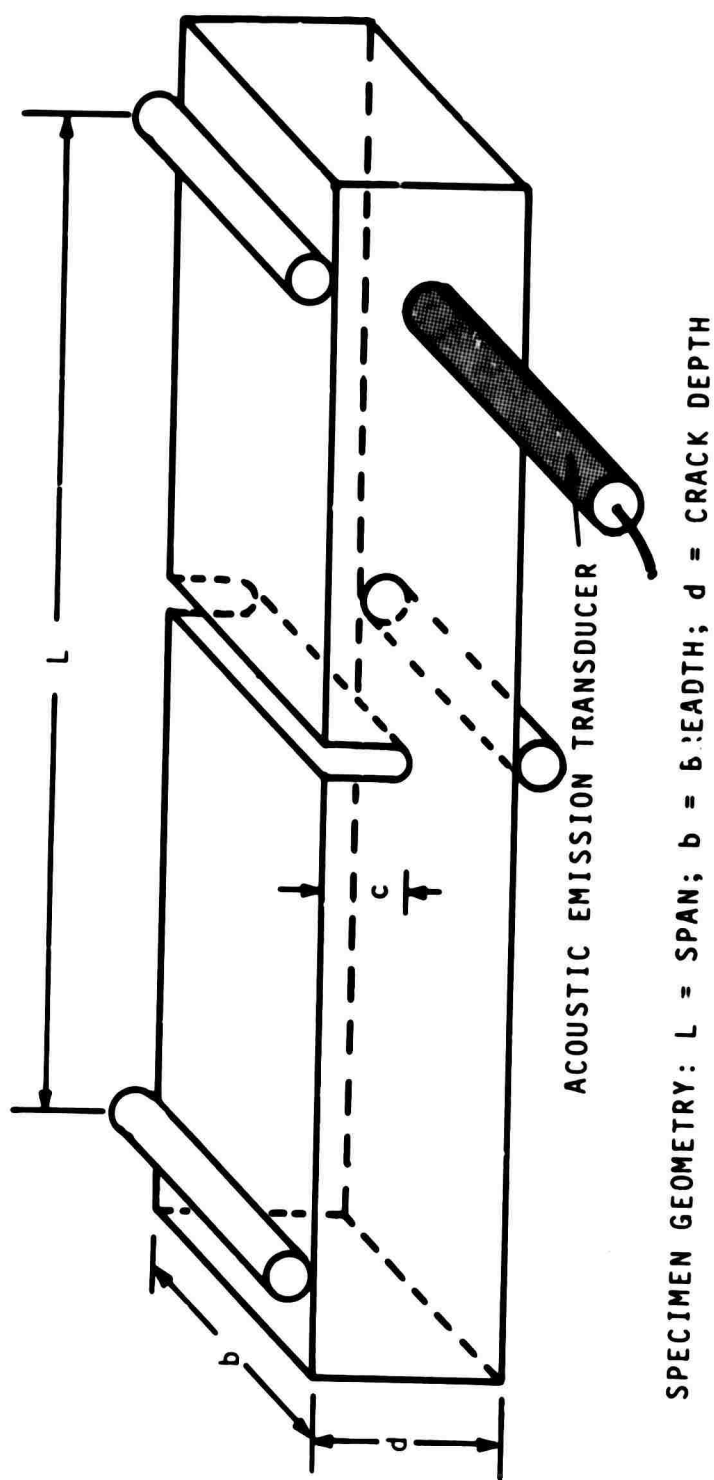
**FIGURE 8.** Micrograph showing 4 Kg Indentations in "Carbone Vitreux" Material. Indentations appear to contain more cracks than in Figure 7.

NOT REPRODUCIBLE

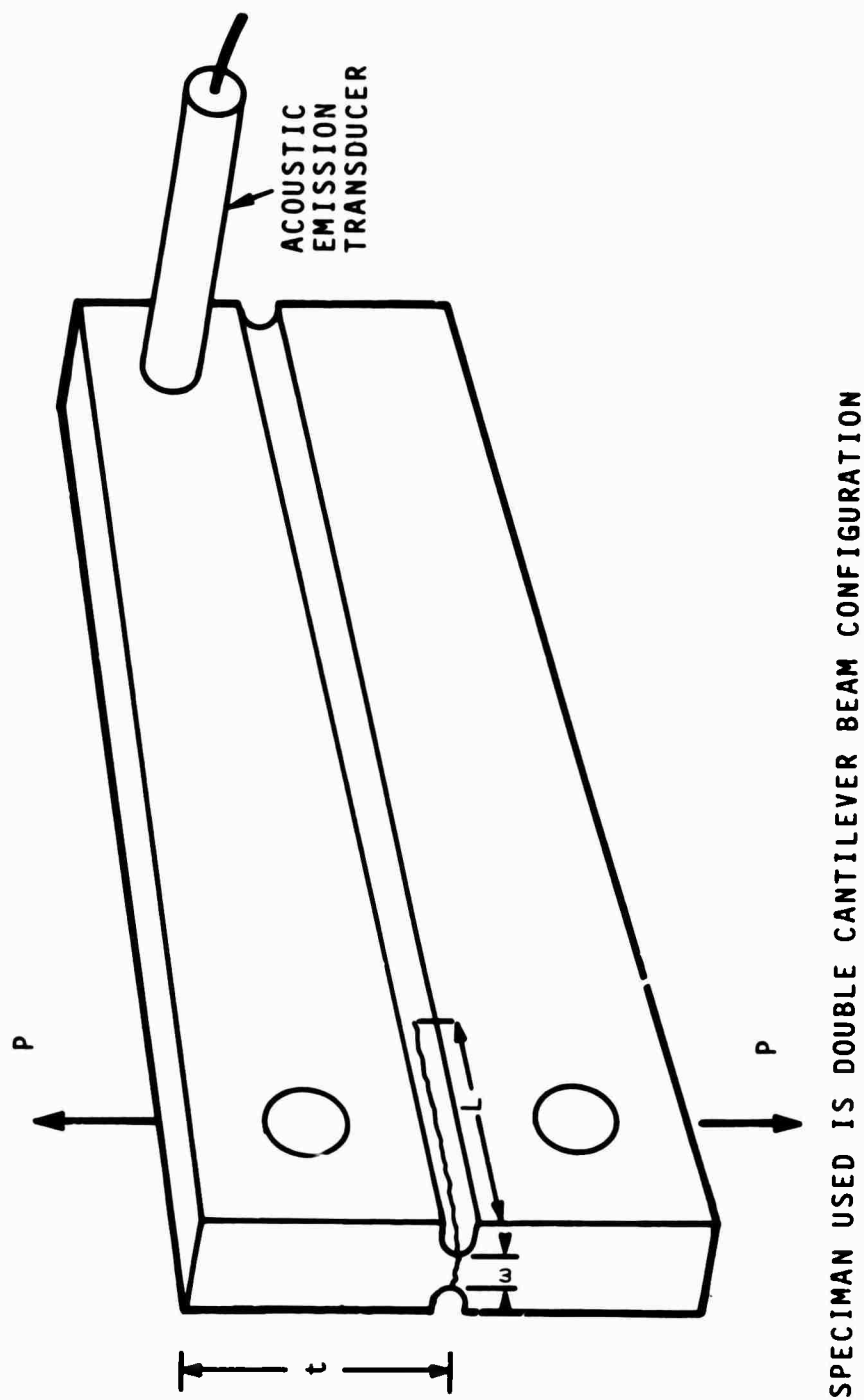


160X

FIGURE 9. Micrograph showing 4 Kg Indentations in Porous Carbon. Little actual cracking appears to have taken place, perhaps more deformation than in pore-free types in Figures 7 and 8.



**FIGURE 10.** Sample Loading Arrangement for Work of Fracture Testing.



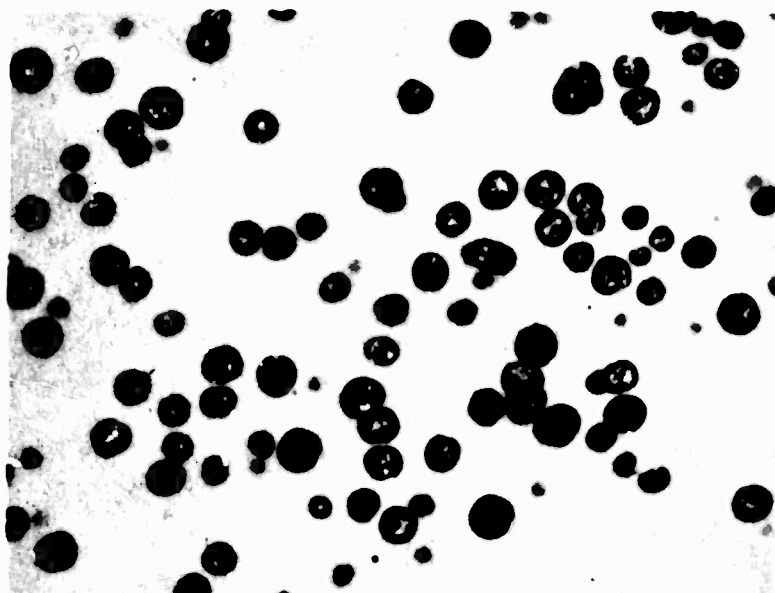
**FIGURE 11.** Sample Loading Arrangement for Fracture Surface Energy Testing.

NOT REPRODUCIBLE



75X

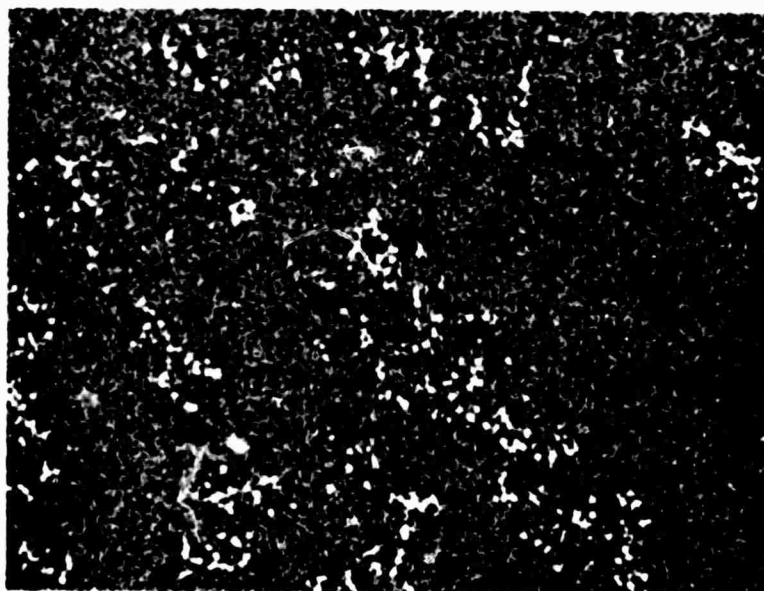
FIGURE 12. Micrograph showing Cross Section of As-Received Carbone Vitreux Sample at Heat Treated at 1000°C.



1000X

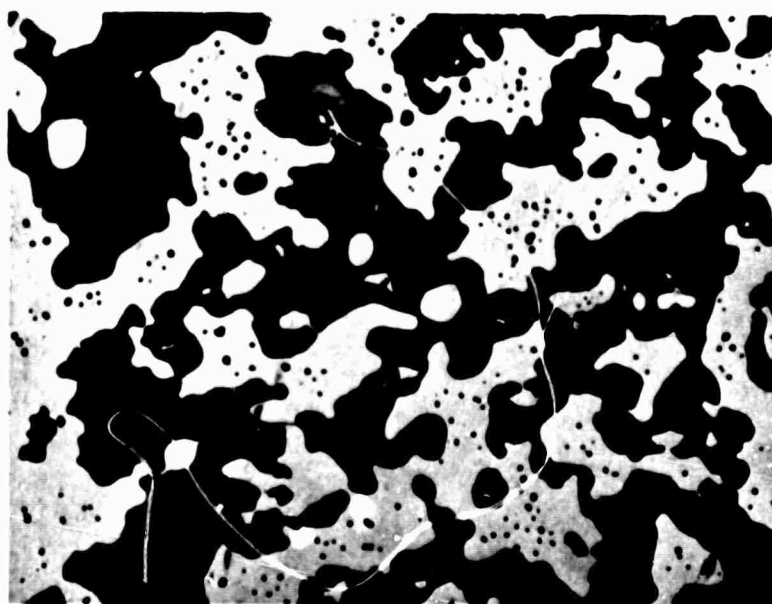
FIGURE 13. Micrograph showing Pore Filling in Carbone Vitreux after Heating to 2000°C.

NOT REPRODUCIBLE



160X

FIGURE 14. Micrograph of Porous Glass-Like Carbon Sample 317-39A, showing Very Fine Pores and Dense Regions.

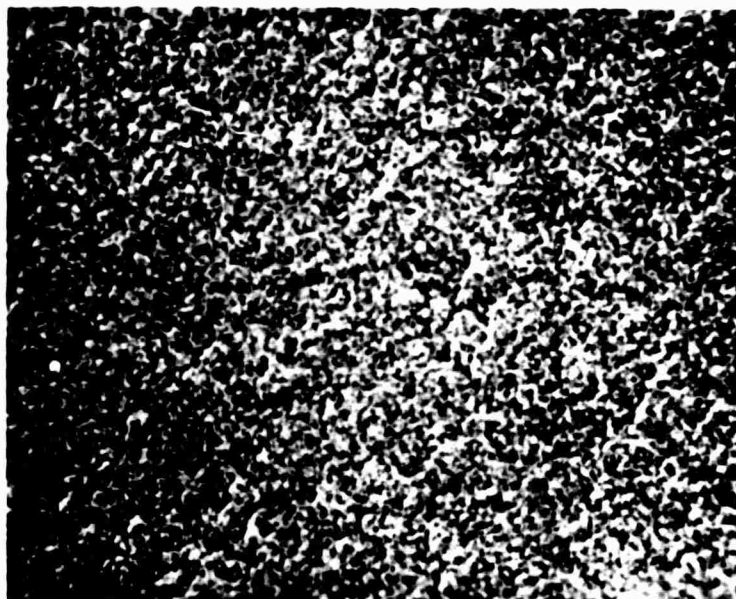


160X

FIGURE 15. Micrograph of Porous Glass-Like Carbon Sample 318-1, showing Large Porosity, Course Structure. The white areas are probably an isostated impurity.

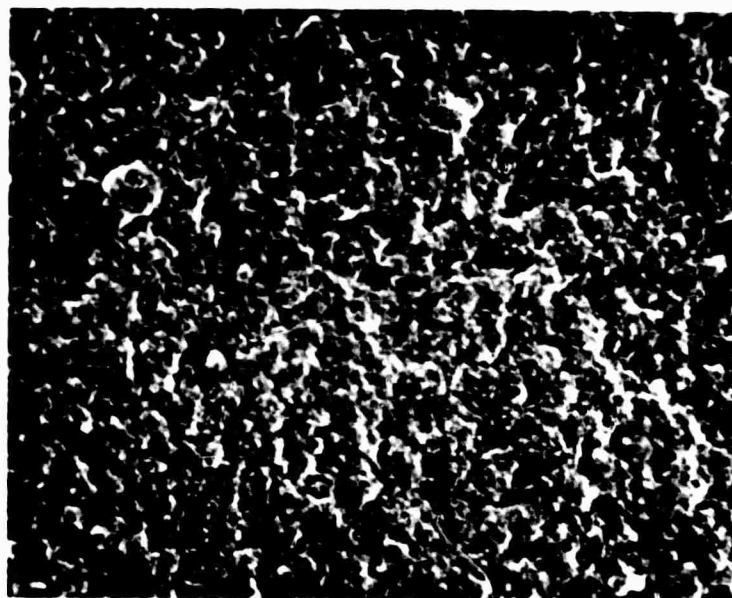


NOT REPRODUCIBLE



10,000X

FIGURE 16. Scanning Micrograph of "Glassy" Carbon Processed at 1000°C. (GC-10) Note nodular structure.



10,000X

FIGURE 17. Scanning Micrograph of "Glassy" Carbon Processed at 3000°C. (GC-30) Note coursening of nodular structure.

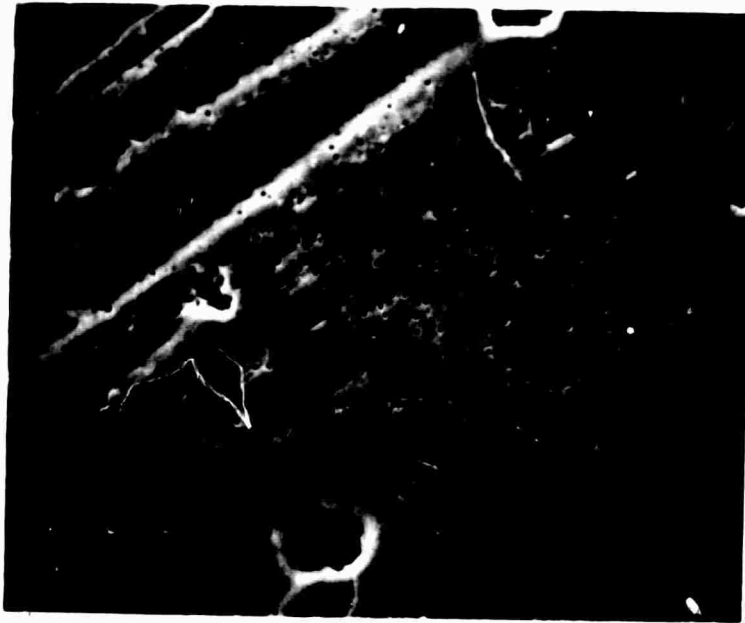
NOT REPRODUCIBLE



300X

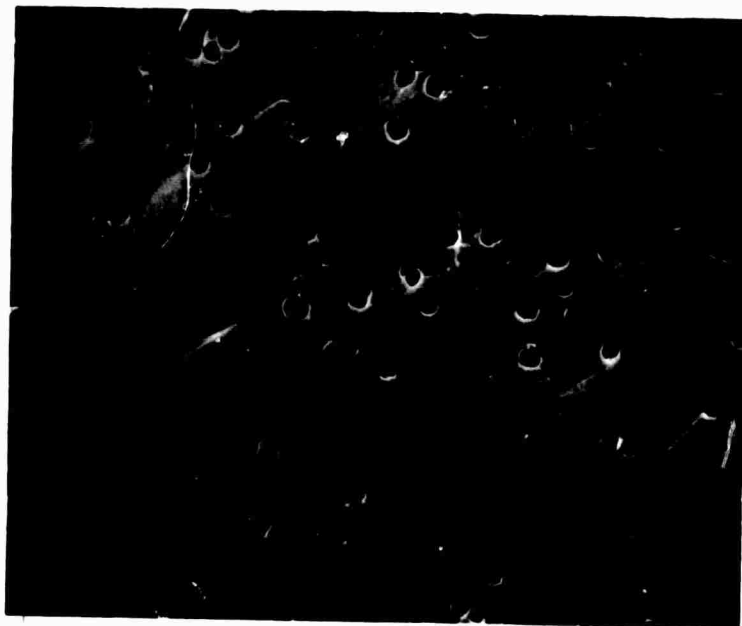
**FIGURE 18.** Scanning Micrograph of 3000°C "Glassy" Carbon (GC-30) showing Prominent Hackle Marks on Fracture Surface.

NOT REPRODUCIBLE



300X

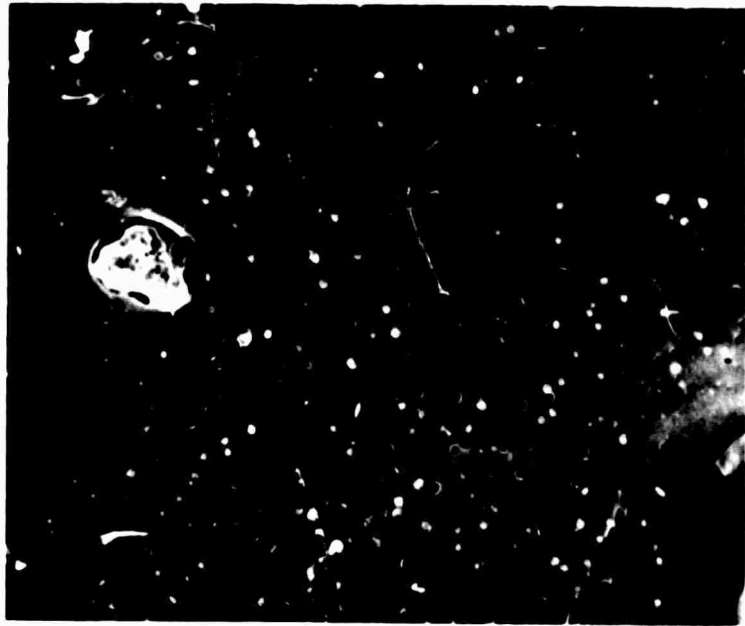
**FIGURE 19.** Scanning Micrograph of 1000°C Carbone Vitreux Fracture Surface.



1000X

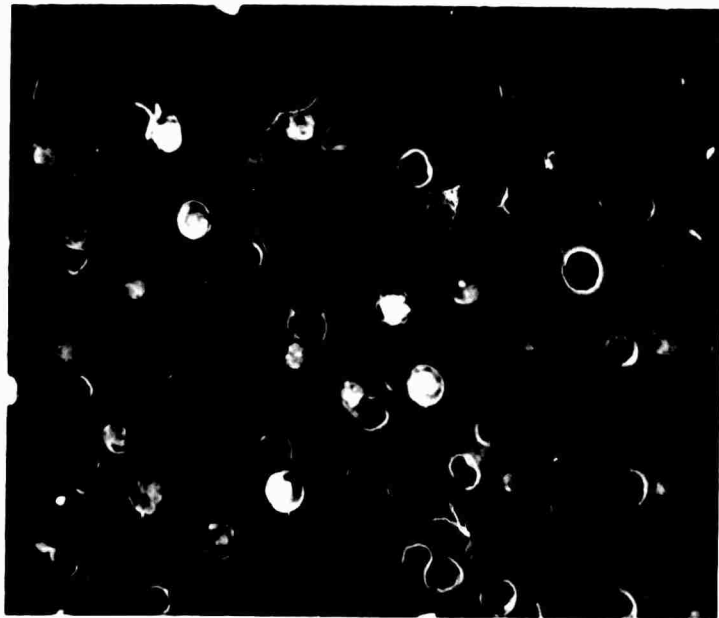
**FIGURE 20.** Scanning Micrograph showing Details of Fracture in Figure 19. Note crack interruptions near pores.

NOT REPRODUCIBLE



300X

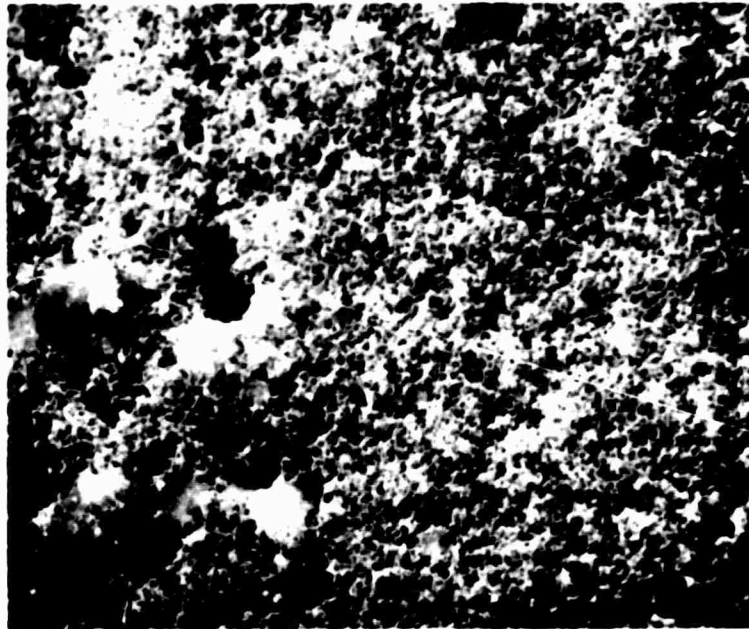
FIGURE 21. Scanning Micrograph of 2900°C Carbone Vitreux Fracture Surface.



1000X

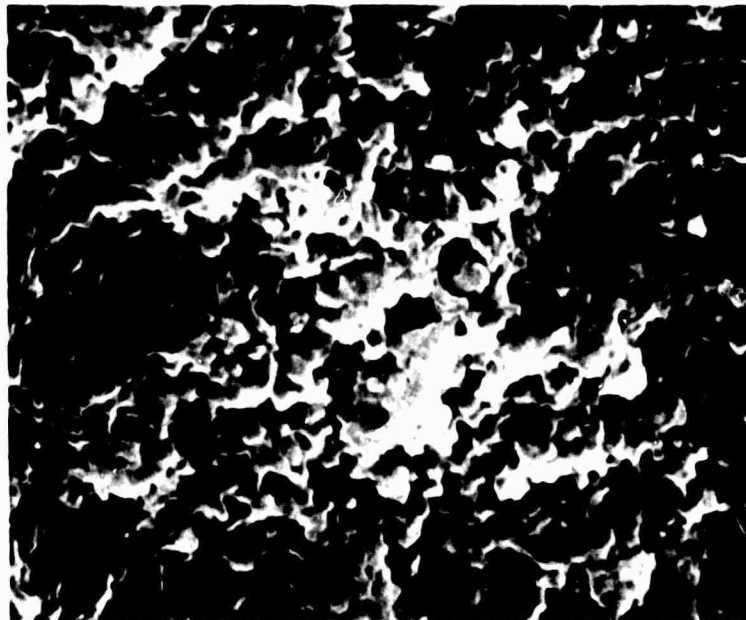
FIGURE 22. Scanning Micrograph showing Details of Fracture in Figure 21. Note pore filling.

NOT REPRODUCIBLE



1000X

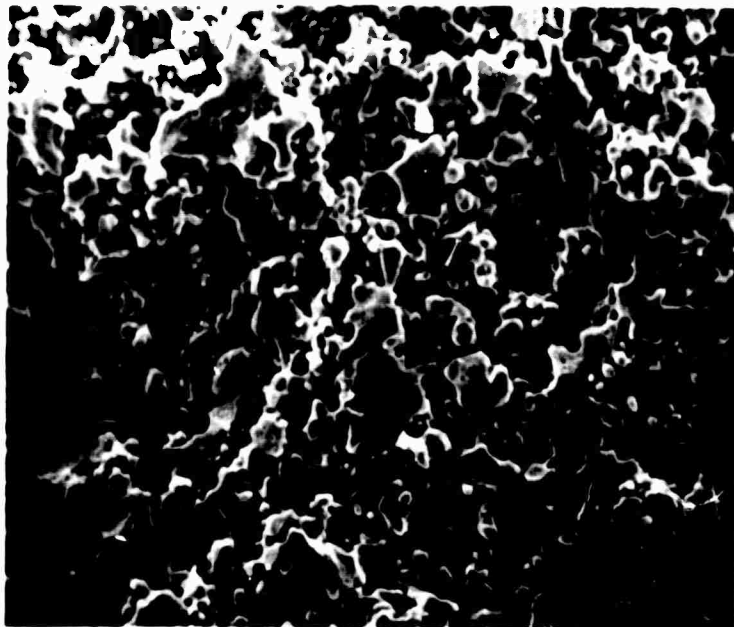
FIGURE 23. Scanning Micrograph showing Porous Carbon Sample 317-39A. Dense regions can be seen in mostly porous material.



10,000X

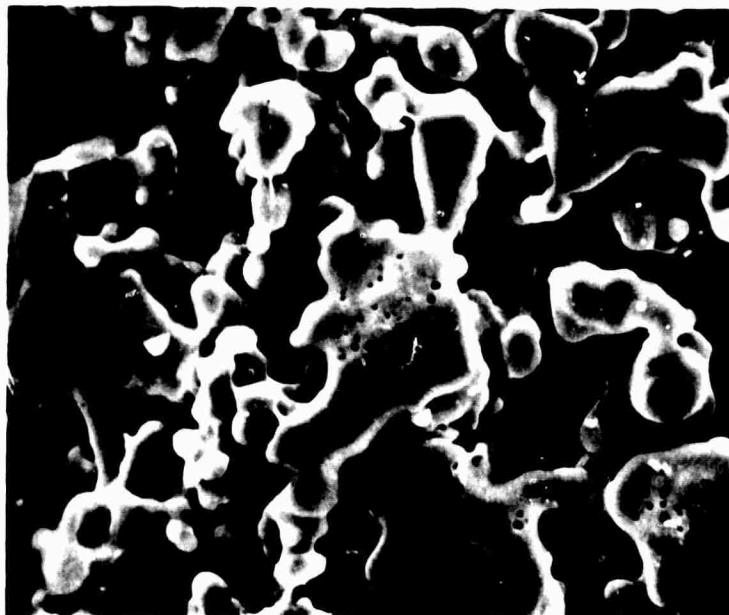
FIGURE 24. Scanning Micrograph showing Fine Porosity in Porous Sample 317-39A.

NOT REPRODUCIBLE



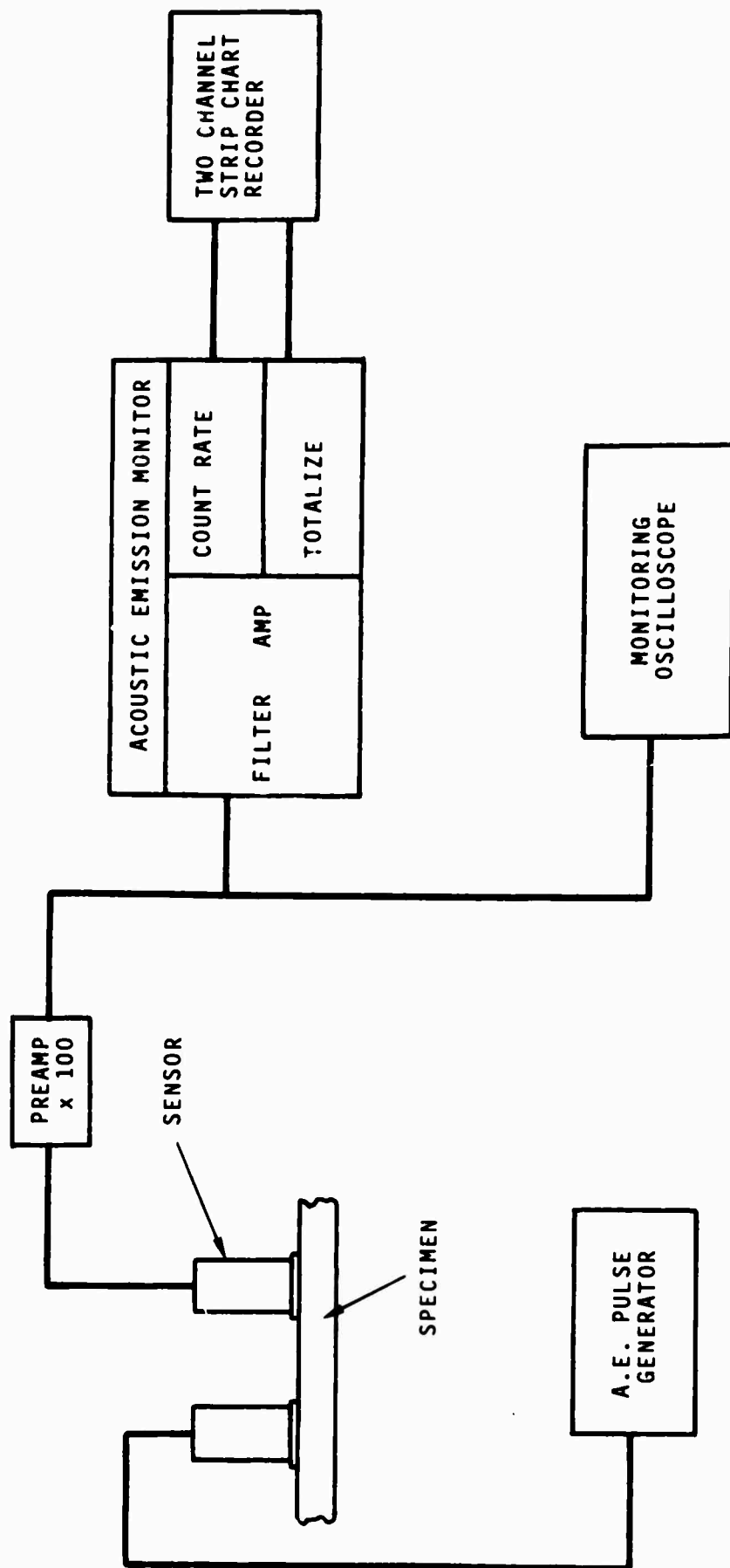
300X

FIGURE 25. Scanning Micrograph showing Course Structure of Porous Carbon Sample 318-1.



300X

FIGURE 26. Scanning Micrograph showing Details of Figure 25. Note small porosity within carbon.



**FIGURE 27.** Block Diagram for Acoustic Emission Monitoring System.

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